

LAMP RELIABILITY STUDIES FOR IMPROVED  
SATELLITE RUBIDIUM FREQUENCY STANDARD

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ABSTRACT

In response to the premature failure of Rb lamps used in Rb atomic clocks onboard Navstar GPS satellites The Aerospace Corporation has initiated experimental and theoretical investigations into their failure mechanism. The primary goal of these studies is the development of an accelerated life test for future GPS lamps.

At this time the primary failure mechanism has been identified as consumption of the lamp's Rb charge via direct interaction between Rb and the lamp's glass surface. The most effective parameters to accelerate the interaction between the Rb and the glass are felt to be rf excitation power and lamp temperature. Differential scanning calorimetry is used to monitor the consumption of Rb within a lamp as a function of operation time. This technique has already yielded base line Rb consumption data for GPS lamps operating under normal conditions.

In order to insure acceleration methods do not alter the mechanism of the Rb-glass interaction detailed surface studies yielding information about the mechanism of interaction are in progress. It has been found that penetration profiles of Rb into pyrex surfaces can be analyzed in terms of one-dimensional diffusion models. Diffusion coefficients may be extracted via these models. The surface studies also indicate that Rb exists in at least two forms in pyrex, a thin colored surface layer and the major colorless penetration component. Further experiments are in progress to extend these results to a wide variety of glasses.

INTRODUCTION

Rubidium (Rb) atomic frequency standards are currently in use onboard Navstar Global Positioning System (GPS) satellites. The premature failure of several of the satellite-borne devices has been attributed to the failure of the Rb lamps used for optical pumping in the Rb clocks. The Aerospace Corporation has responded to these events by initiating investigations into Rb lamp failure mechanisms. The primary goal of these studies is to develop an acce-

lerated life test to insure the reliability of future GPS Rb lamps. The test must be such that its application for a reasonable period of time will indicate that under normal operating conditions the Rb lamp will function for the required GPS mission lifetime.

There are several steps involved in developing such an accelerated life test:

- i) Identify the primary lamp failure mechanism
- ii) Determine the factors which accelerate this mechanism and quantify their effects
- iii) Insure that the acceleration procedure does not alter the failure mechanism.

In the body of this paper our results in each of these areas are discussed.

## II. FAILURE MECHANISM IDENTIFICATION

The GPS Rb lamps are of the standard Bell, Bloom, and Lynch [1] electrodeless discharge design. The current envelopes, composed of Corning 1720 glass, are cylindrical, approximately 1 cm in diameter and 2 cm in length. They contain both rare gas buffer, xenon (Xe), and an excess Rb metal charge which has a current GPS specification of from 300 to 500 $\mu$ g. During operation, the base of the lamp, which is its coldest point, is thermostated to the desired temperature to maintain constant Rb vapor pressures.

Several possible failure mechanisms may be proposed. It can be suggested that the electronically excited Rb is being quenched by vapor phase impurities prior to radiative emission. These impurities result from glass envelope outgassing. Another possibility is that outgassed impurities, for example water (H<sub>2</sub>O) or oxygen (O<sub>2</sub>), react directly with atomic Rb converting the lamp's Rb charge to nonvolatile compounds. The consumption of Rb charge through either reaction with or diffusion into the lamp envelope is also possible. Finally, the actual failure process may be some combination of the above mechanisms.

### A. Quenching of Excited Rubidium

A number of experimental results indicate that quenching of the excited atomic Rb is not significant. Emission spectra from both good and failed lamps have been obtained with a 3/4 m spectrometer and analyzed over the spectral range from 400 nm to 800 nm. Literally hundreds of lines are assigned to either atomic transitions

of Xe, Rb, or trace amounts of potassium and cesium normally found as impurities in the Rb. In the failed lamps only emission lines present in good lamps were observed. No emission lines from possibly outgassed impurities such as hydrogen ( $H_2$ ), nitrogen ( $N_2$ ), or  $O_2$  were detected. These results are consistent with and absence of quenching species.

Comparisons of emission intensities of the Rb 780.0 nm line and the Xe 823.2 nm line as functions of lamp base temperature for both good and failed lamps are shown in Figure 1. In addition, the Rb vapor pressure curve is plotted on Figure 1a. At low base temperature ( $< 100^\circ C$ ) Xe emission intensities are the same for both good and failed lamps. This indicates that the rf discharge has not changed due to the failure of the lamp. The most obvious difference between the good and failed lamps is that the Rb emission intensity is less in the failed lamp. The magnitude of the intensity reduction varies among failed lamps, depending on how far the failure process has proceeded. In Figure 1b the failed lamp's Rb intensity is nearly three orders of magnitude lower than that of a typical good lamp.

A reduction in emission intensity could result from quenching, however, careful examination of these curves shows conclusively that quenching is not significant in failed lamps. If quenching were the only process occurring, the entire Rb emission versus temperature curve would be expected to shift to lower magnitudes. This is not observed. While the Rb emission intensity of the good lamp increases monotonically (for temperatures less  $140^\circ C$ ) as the lamp base temperature is increased, the failed lamp displays nearly constant Rb intensity over the  $20^\circ C$  to  $70^\circ C$  range. This constant intensity portion of the curve implies the existence, in failed lamps, of a mechanism yielding vapor phase Rb which is essentially temperature independent. If rather than quenching, a reduced vapor phase density causes the diminished Rb intensity in failed lamps, the relative magnitude of Rb released by the temperature independent mechanism would be small compared to normal vaporization. It is speculated that the temperature independent mechanism may involve release of Rb imbedded in the glass via a plasma sputtering process.

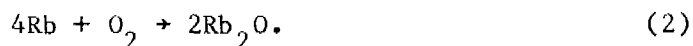
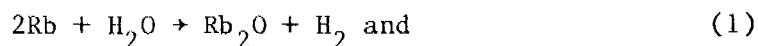
At temperatures where the Rb vapor density is low enough so that self-absorption is not significant, ( $< 100^\circ C$ ), the emission intensity of a good lamp follows the vapor pressure curve closely. As the temperature,  $T$ , increases (above  $100^\circ C$ ) the emission intensity begins to drop below the vapor pressure curve due to increasing self-absorption. However, Rb emission from the failed lamp ( $110^\circ < T < 150^\circ$ ) displays no slope change due to self-absorption. Since self-absorption should not be affected by quenching it appears that the vapor density of Rb in a failed lamp is significantly lower than in a good lamp. At approximately  $145^\circ C$  the emission intensities on

Figure 1a change dramatically. This happens as the plasma changes from a mixed mode in which both Rb and Xe are excited to a Rb only mode in which Rb is primarily excited. This mode change is found to be dependent on the Rb vapor density. At a specified rf excitation power the plasma will change to a Rb only mode when the Rb vapor pressure has reached a sufficient level. Looking at Figure 1b no mode change is observed to occur. This is again consistent with a reduced Rb vapor density in a failed lamp.

Finally, applying the integrated form of the Clausius-Clapeyron equation [2] to data of the type found on Figure 1 allows determination of the heat of vaporization of Rb in both good and failed lamps. For good lamps the experimental heat of vaporization is found to be  $18.1 \pm 0.3$  kcals per mole. The reported value for elemental Rb is 18.11 kcals per mole [3]. However, for failed lamps the heat of vaporization is found to be  $23.9 \pm 0.2$  kcals per mole. This implies that a liquid reservoir of Rb is not present in the failed lamp. Quenching, if it occurred, would not affect the heat of vaporization. Consequently, lamp failure results from a lack of Rb rather than its quenching.

#### B. Rubidium Reaction with Impurities

The second postulated mechanism for the failure of Rb lamps in the GPS Rb frequency standard is the loss of Rb by reaction with species outgassed from the glass envelope to form nonvolatile rubidium oxide ( $\text{Rb}_2\text{O}$ ). The most likely reactions are,



Experiments which tested for the presence of  $\text{H}_2$  in failed lamps prove that reaction with  $\text{H}_2\text{O}$  is not significant. Rf-induced emission spectra from a series of standard lamps containing  $\text{H}_2$  and Xe were analyzed to obtain a detection limit of  $\text{H}_2$  in the presence of the Xe buffer. Comparison of these spectra with those of failed lamps indicates that the pressure of  $\text{H}_2$  in a failed lamp is less than 1 torr. A subsequent removal of the evolved  $\text{H}_2$  through either formation of rubidium hydride,  $\text{RbH}$ , or permeation through the glass envelope has been ruled out.  $\text{RbH}$  is known to photodissociate when exposed to UV radiation [4], such as found in abundance within the lamp due to numerous Xe transitions. The permeation velocity constant for  $\text{H}_2$  [5, 6] is too low to allow for a significant loss of  $\text{H}_2$  through the glass. Thus less than  $10\mu\text{g}$  of rubidium could be consumed by the postulated mechanism.

The fact that the amount of water desorbed from the glass envelope does not consume a significant amount of Rb has a bearing on the importance of reaction 2. Todd [7] states that the gas evolved from glasses of temperatures below their softening points is primarily water. Todd's studies covered a wide range of glasses including Corning 1720. His results are also consistent with data presented by Dushman [8] which indicate  $H_2O$  outgassing is greater than that of  $O_2$ . A question arises whether  $O_2$  outgassing might be preferentially accelerated by the rf discharge present in the lamp. Studies of electron bombardment of glass surfaces indicate this bombardment can release  $O_2$  [9, 10]. However, keV electrons were required to induce significant outgassing. From spectroscopic measurements the average kinetic energy of the electrons in the GPS lamp discharge is estimated to be less than 1 eV. In light of this information it is strongly believed that insufficient  $O_2$  is released by the lamp envelope to consume any significant amount of Rb.

#### C. Interaction of Rubidium with Glass

It has long been reported in the literature that alkali vapors react directly with glass surfaces [11-13]. Glasses exposed to alkali vapors are known to discolor as the interaction processes proceed. Failed GPS lamps display this discoloration implying reaction of Rb with the glass envelope. In light of this, surface analysis techniques have been applied to lamp envelopes. They indicate that Rb penetrates many micrometers into the glass. On the vapor-exposed surface the Rb's chemical form is found to be similar to that of an oxide or silicate, again implying reaction with the glass. In light of these results, it is believed that the primary failure mechanism in GPS lamps is the consumption of Rb via its direct interaction with the lamp's glass envelope. The mechanisms of this interaction are discussed in terms of the surface analysis studies in Section IV.

### III. ACCELERATION PARAMETERS AND QUANTIFICATION OF RUBIDIUM CONSUMPTION

#### A. Acceleration Parameters

With the identification of the primary failure mechanism it is possible to suggest parameters to accelerate the mechanism. Two such parameters under current investigation are lamp temperature and rf excitation power. Whether the interaction is a simple reaction whose rate is dependent on a rate constant,  $k$ , or a more complicated process involving diffusion effects characterized by a diffusion coefficient,  $D$ , the temperature would be expected to play an important role.

In the simplest approximation, rate constants, in general, obey the following proportionality,

$$k \propto \exp(-\Delta E/RT) \quad (3)$$

where  $\Delta E$  is the activation energy for the reaction of interest,  $R$  is the gas constant, and  $T$  is the absolute temperature. Over limited temperature ranges (several hundred °C) diffusion coefficients have been found to obey a similar proportionality,

$$D \propto \exp(-Q/RT) \quad (4)$$

where  $Q$  is an effective activation energy for the diffusion process. For both  $k$  and  $D$ , increasing temperature increases their magnitudes and due to their exponential relation to temperature this increase may be rapid. An increase in temperature may increase the interaction between Rb and glass in an additional manner. A higher reservoir temperature will cause a higher Rb vapor density resulting in the more rapid consumption of Rb via either a reactive or diffusive mechanism.

To aid in understanding the effects of rf excitation power and the plasma itself on the interactions of Rb vapor with the lamp envelope theoretical modeling of the plasma has been carried out. This model assumes electron production takes place in the lamp plasma by electron impact with Rb atoms. Electron loss is assumed to occur via ambipolar diffusion to the wall and subsequent recombination of electrons and ions. With these assumptions rate equations for the populations of the atomic and ionic Rb species may be set up. Solution of those equations in a cylindrical geometry yields atomic Rb and electron densities as a function of radial position. The salient results of these calculations are shown in Figure 2 [14].

In Figure 2a and b the left-hand ordinate describes the electron density while the right-hand ordinate gives the Rb density. The glass wall occurs at  $r = 4$  mm. In the absence of the Rb discharge the distribution of Rb atoms is given by the dashed lines. In Figure 2a, for 0.3 W/cm rf power the calculation yields a Rb atom density at the wall of approximately  $3.5 \times 10^{14}$  atoms/cc. This is 3.5 times the nonplasma density of  $1 \times 10^{14}$  atoms/cc. The results for an rf excitation power of 3 W/cm are shown in Figure 2b. In this case the presence of the plasma increases the wall Rb atom density by more than a factor of nine over the nonplasma density. It is seen that with increasing rf power into the plasma the concentration of Rb at the lamp wall also increases. This higher density will accelerate the consumption of Rb whether the interaction mechanism is reaction, diffusion or a combination of both.

## B. Experimental Determination of Rubidium Consumption

It is expected that both temperature and rf power will be useful in accelerating the interaction of Rb with the glass envelope. To establish these acceleration effects the baseline Rb consumption rate for GPS lamps operating in normal environments must be determined. However, in order to obtain this rate it is first necessary to develop a technique to monitor Rb consumption within a lamp.

In the current experiments the technique of differential scanning calorimetry (DSC) has been used to determine the amount of Rb contained within GPS lamps. This technique to measure the Rb content in a lamp was first proposed by workers at EG & G, Inc. [15]. In DSC, sample and reference objects are both heated such that their temperatures increase at the same rate. Heating rates are measured in °C/min. The instrument measures the heat flow, in calories per minute, required to maintain this heating rate for both sample and reference. The difference between these two heat flows is the instrument output, which is typically plotted versus time.

The sample object is a GPS lamp while the reference is a GPS lamp envelope containing no Rb. When the melting point of Rb (38.9°C) is reached, the excess heat required to melt the Rb contained in the sample lamp appears as a peak on the heat difference versus temperature plot. The area of this peak can be equated to the heat required to melt the Rb and division of this heat by Rb's heat of fusion, 6.14 cal/gram, yields the lamp's Rb content. Figure 3 is a typical DSC curve for a Rb lamp. Rb content is typically determined to ± 10% at 100 µg and ± 50% at 10 µg.

The DSC technique has been applied to GPS lamps operating in both vacuum and normal atmospheric pressure under standard temperature and rf power conditions. No significant difference in rate of Rb consumption between vacuum and atmospheric operation has yet been observed. Consequently in Figure 4, consumption data as a function of running time for lamps operating in both environments have been combined.

In Figure 4, the data span operating times from several hundred hours to 5,000 hours. The amount of Rb consumption can be fit to a power relation of the form,

$$M_{\text{Rb}} = 1.1 t^{0.54}, \quad (5)$$

where  $t$  is the operation time in hours and  $M_{\text{Rb}}$  is the amount of Rb consumed in micrograms.

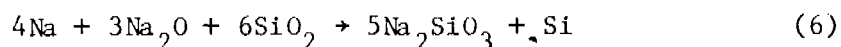
Currently, Rb consumption is being monitored for lamps under normal conditions, elevated temperatures, and high rf powers to ascertain whether accelerated consumption can indeed be induced. At this point the result of these studies are still preliminary and will not be discussed.

#### IV. MECHANISMS OF THE RUBIDIUM-GLASS INTERACTION

##### A. Results of Previous Investigations

As Rb lamps are subjected to a wider variety of operating conditions in an attempt to accelerate the Rb-glass interaction, care must be taken to insure the interaction mechanism occurring under normal operating conditions is not altered. To accomplish this a detailed knowledge of this mechanism must be obtained. Prior to our investigations very little work had been aimed at understanding the Rb-glass interaction. The majority of alkali-glass studies have focused on the sodium (Na)-glass interaction which occurs much more rapidly than Rb-glass processes. It is interesting to note that a major rationale of the prior investigations has been the possible improvement of alkali vapor lamps. However, virtually none of the previous studies has been conducted with an electrical discharge present.

In the case of Na, the consensus is that no single mechanism explains its interaction with glass [16-18]. Typically, one of two effects is observed. The first effect often occurs in glasses with high SiO<sub>2</sub> content. Exposure to Na results in the formation of a brown crystalline layer containing nearly 20% Na by weight [16]. The edge of this layer is found to advance into the glass at a rate proportional to the square root of the time of exposure [16], which is consistent with a Na-glass reaction limited by a diffusion-controlled step [19-20]. Elyard and Rawson [12] have suggested several reactions which are thermodynamically favored resulting in a variety of sodium silicates. Using x-ray diffraction, Brinker and Klein [16] have shown the crystalline phase was sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>). Consequently, they suggest that the most probable of Elyard and Rawson's proposed reactions is the following,



$$\Delta G_{400^\circ\text{C}} = 1583 \text{ KJ/mole.}$$

The second effect, typically observed in glasses containing less than 70% (mole) SiO<sub>2</sub> [16], is characterized by a brownish discoloration of the glass. The discolored glass has apparently not undergone any devitrification and the crystalline material observed in the first effect is not present. The discoloration is described



as advancing into the glass with a sharp boundary [16]. This boundary has also been observed to advance into the glass at a rate proportional to the square root of time, again indicating a diffusion-controlled process. Brinker and Klein [16] believe that this process is the result of atomic Na diffusing into the glass.

What information may be drawn from the previous studies of the Na-glass interactions and applied to Rb's interactions with Corning 1720? Corning 1720 is a calcium aluminosilicate glass [21] containing less than 70% (mole)  $\text{SiO}_2$ . While this seems to imply the second effect would be most likely, care must be exercised. Corning 1720 also contains aluminum and boron oxides ( $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ ). The presence of these modifiers can significantly affect how a glass reacts when exposed to Na and most likely to Rb. Further, the parameters of greatest interest, the rates of Rb consumption, are not obtainable from the previous Na studies. Consequently, investigations specifically aimed at understanding Rb-glass interactions are required.

#### B. Current Surface Analysis Studies

In Figure 5, a "typical" Na penetration profile is compared to a Rb penetration profile representative of those currently being analyzed. Na-glass studies generally immersed glass samples in liquid Na at elevated temperatures. A profile similar to Figure 5a results when a glass sample is placed in  $400^\circ\text{C}$  Na for about 100 hours. Due to the rapidity of its progress into the glass, the Na profile can be followed using absorption spectroscopy, magnified examination of a glass cross section, or wet chemical etching techniques. The rate of progress of this penetration front yields the Na diffusion coefficient. In contrast, the reaction of Rb with glass under the conditions of current interest is orders of magnitude slower than that of Na. Exposure of glass to Rb vapor, whose density is specified by the Rb vapor pressure at temperatures near  $200^\circ\text{C}$ , for several thousand hours will yield a Rb profile similar to that in Figure 5b. In this case it is necessary to analyze the functional form of the profile rather than the penetration depth to determine the diffusion coefficient.

##### 1. Secondary Ion Mass Spectrometry (SIMS) Studies

To obtain the highly accurate penetration profiles needed to analyze Rb permeation of glass the technique of SIMS has been applied to cross-sectional pieces of Rb-exposed lamp walls. In the SIMS technique a  $1.5\ \mu\text{m}$  diameter beam of oxygen ions is aimed at the sample. Secondary ions sputtered from the surface are mass spectrometrically analyzed allowing determination of elemental composition. Our initial tests were performed on Rb lamp with pyrex envelopes under plasma and nonplasma conditions. In both cases lamps

were thermostated in oil baths to maintain constant vapor pressures. Pyrex was selected for those studies because it is known to react with alkali vapors.

Figure 6 shows the raw SIMS profiles of silicon (Si) and Rb for a lamp exposed to a plasma discharge. Zero micrometers is the inner surface of the lamp wall. The gradual increase of Si and Rb concentrations near zero is due to the finite width of the SIMS beam. Treating these data as simple one-dimensional diffusion allows fitting them to the form [20]

$$\frac{C(X,t)}{C_0} = \operatorname{erfc} \frac{X}{\sqrt{4 D t}}, \quad (7)$$

where  $X$  is the penetration depth,  $t$  is the exposure time,  $C_0$  is Rb concentration at the wall, and  $D$  the diffusion coefficient resulting from the fitting process.

Experimental Rb data along with fit curves for pyrex lamps with and without plasma present are given in Figure 7. In both cases the diffusion coefficient is approximately  $3 \times 10^{-14} \text{ cm}^2/\text{sec}$ . This is in good agreement with high temperature diffusion coefficient data [22] extrapolated into the low temperature regime (about  $140^\circ\text{C}$ ).

The SIMS Rb penetration profiles indicate that Rb has penetrated many micrometers into the glass. This is particularly clear in Figure 7b whose sample was exposed to Rb vapor for a longer period of time than that of Figure 7a. The depth of Rb penetration cannot be attributed to a smearing of the true profile resulting from the finite width of SIMS ion beam. This beam, which is only approximately 1.5 micrometers in diameter, would smear a surface layer to a depth of at most 2 micrometers. In fact, in Figure 7b the amount of Rb which has diffused beyond 2 micrometers is greater than the amount found in this surface region.

Analysis of the SIMS data yields support for the theoretical plasma model. Using only vapor pressure/temperature considerations results in a ratio of the vapor density at the glass surface with plasma present,  $P_p$ , to the vapor density at the glass surface for the nonplasma sample,  $P_{np}$ , equal to approximately 0.1. However, if the plasma model is correct, the vapor density at the glass surface in the plasma case should be higher than expected from vapor pressure considerations. This could result in a larger  $P_p/P_{np}$  value. Integrating the SIMS curves allows determination of the total amount of Rb which has penetrated the glass. Combining these amounts with the extracted diffusion coefficients, the known exposure times, and the one-dimensional diffusion model allows calculation of the relative vapor densities exposed to the glass surfaces with and without plasma

present. The experimental  $P_p/P_{np}$  ratio is found to be approximately 1. The fact that this ratio is larger than would be predicted by only vapor pressure/temperature considerations is consistent with the plasma model predictions.

## 2. Electron Spectroscopy for Chemical Analysis (ESCA) Experiments

The chemical form of the Rb within the glass has been investigated using ESCA. In this method the surface of the sample is exposed to monochromatic X-rays and the photoejected electrons are energy analyzed. The resulting core electron binding (ionization) energies are characteristic of both a given element and its chemical form.

Table I summarizes the current ESCA results. Pure rubidium hydroxide (RbOH) and  $Rb_2O$  were analyzed as standards. Pyrex samples exposed to Rb were also analyzed. These pyrex samples had a yellow-brown discoloration as long as they were kept in dry atmospheres. However, upon exposure to moist air they became colorless in a matter of seconds. The rapidity of this discoloration indicates Rb exists in a colored form on a thin surface layer, probably less than  $0.1 \mu m$  thick. However, from the SIMS data it was seen that most of the Rb has diffused into the glass many micrometers. Consequently, Rb exists in at least two forms in pyrex. The minor form is a colored surface layer, while the major form extending more deeply into the glass is not significantly colored. The ESCA studies have thus far yielded information about the surface layer. Prior to water vapor exposure the Rb in the surface layer of pyrex is similar in form to a rubidium oxide or possibly a rubidium silicate. However, on exposure to moist air it becomes RbOH.

Currently, it appears the interaction mechanism between Rb and a glass surface is not dependent on whether a plasma is present or not. From this it may be inferred that varying the rf power into the plasma will not significantly affect the nature of the Rb-glass interaction. This will be important if increased rf power does indeed accelerate the interaction. Further, the nature of the diffusive mechanism apparent in these glass samples should not be significantly affected by temperature changes over several hundred degrees Celsius. Consequently, temperature should also be a reasonable acceleration parameter. Additional experiments on different glasses including Corning 1720 at elevated temperatures and rf powers are currently underway to further substantiate these statements.

Table I. ESCA Results

	<u>Rb (3d<sub>5/2</sub> 3d<sub>3/2</sub>)</u> <u>Binding Energy (eV)</u>	
RbOH	109.8 ± 0.2	
Rb <sub>2</sub> O	110.3	
	<u>Non-plasma</u>	<u>Plasma</u>
Rb + Pyrex	110.7	110.5
Rb + Pyrex (Air Exposed)	—	109.8

V. DISCUSSION

The studies described in this paper represent a systematic investigation into the failure mechanisms of one portion of the Rb atomic frequency standard's physics package. The current investigations have resulted in the identification of the primary lamp failure mechanism along with obtaining baseline Rb consumption data for GPS type lamps. Additionally, insights into the mechanisms of the Rb consumption process have been gained. These studies will not only yield an accelerated life test for the GPS program but also allow reliability estimates to be made for Rb lamps. We consider the current investigations to be the first step in understanding the failure mechanisms of, and obtaining reliability estimates for, the entire physics package of the frequency standard.

## REFERENCES

1. W.E. Bell, A.L. Bloom, and J. Lynch, *Rev. Sci. Instr.* 32, 688 (1961).
2. K. Denbigh, *The Principles of Chemical Equilibrium*, Third Edition, Cambridge University Press, London, p. 202, 1971.
3. *Handbook of Chemistry and Physics*, Forty-Ninth Edition, The Chemistry Rubber Company, Cleveland Ohio, D 33, 1968.
4. R. Hilsch, *Ann. Physik.* 32, 155 (1938).
5. F.J. Norton, *J. Am. Ceram. Soc.* 36, 90 (1953).
6. V.O. Altemose, *J. App. Phys.* 32, 1309 (1961).
7. B.J. Todd, *J. Appl. Phys.* 26, 1238, (1955).
8. S. Dushman, *Scientific Foundations of Vacuum Technique*, John Wiley and Sons, Inc., New York, pp. 509-527, 1949.
9. B.J. Todd, J.L. Lineweaver, and J.T. Kerr, *J. Appl. Phys.* 31, 51, (1960).
10. J.L. Lineweaver, *J. Appl. Phys.* 34, 1786 (1963).
11. G.R. Fonda and A.M. Young, *Gen. Elect. Rev.* 37, 331 (1934).
12. C.A. Elyard and H. Rawson, *Advances in Glass Technology*, Plenum Press, New York, p. 270, 1962.
13. W. Happer, *Rev. Mod. Phys.* 44, 169 (1972).
14. H.U. Eckert, a complete presentation of these calculations will be published.
15. T. Lynch, EG & G, Inc., private communication.
16. C.J. Brinker and L.C. Klein, *Phys. Chem. Glass* 21, 1414 (1980); *Phys. Chem. Glass* 22, 23 (1981).
17. A.J. Burggroof and H.C. Van Velzen, *J. Am. Ceram. Soc.* 52, 238 (1969).
18. A.J. Burns, *Glass Technol.* 6, 17 (1965).
19. R.H. Doremus, *J. Non-Cryst. Solids* 25, 263 (1972).

20. J. Crank The Mathematics of Diffusion, Oxford University Press, London, Chapter 8, 1957.
21. Kirk-Othmer Encyclopedia of Chemical Technology, V. 11, M. Grayson ed., John Wiley and Sons, Inc., New York, p. 826, 1980.
22. A. Kolitsch, R. Kuchler, E. Richter, Silikatechnik 29, 369 (1978).

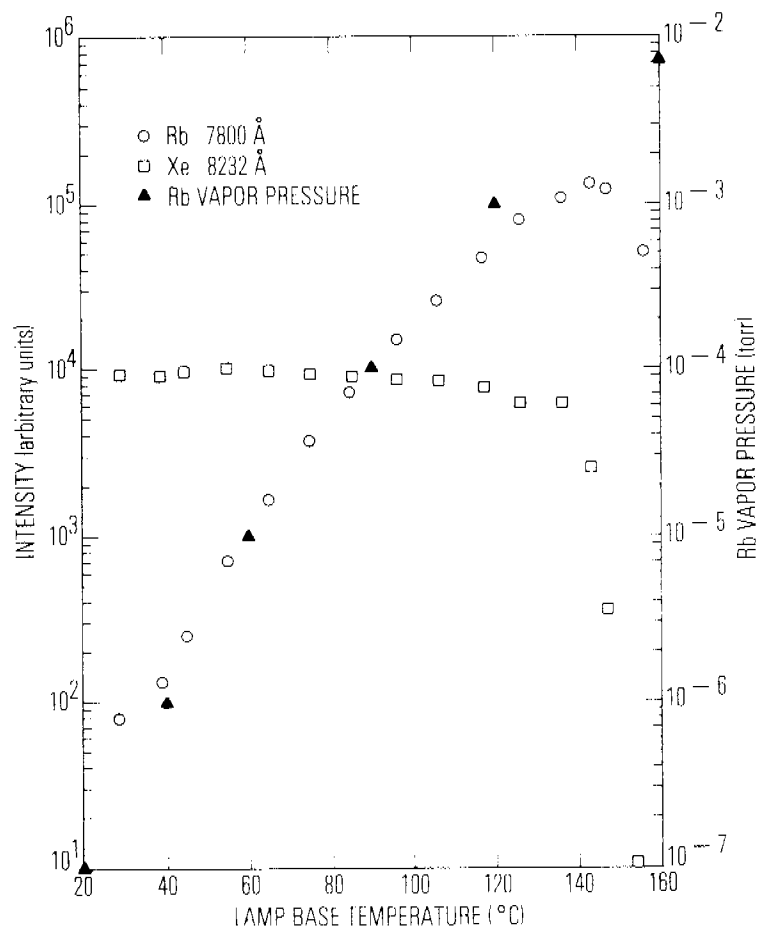


Figure 1a. Emission intensities of Rb 7800Å line (○) and the Xe 8232Å line (□) for a good Rb lamp as a function of base temperature. (▲) are Rb vapor pressure values

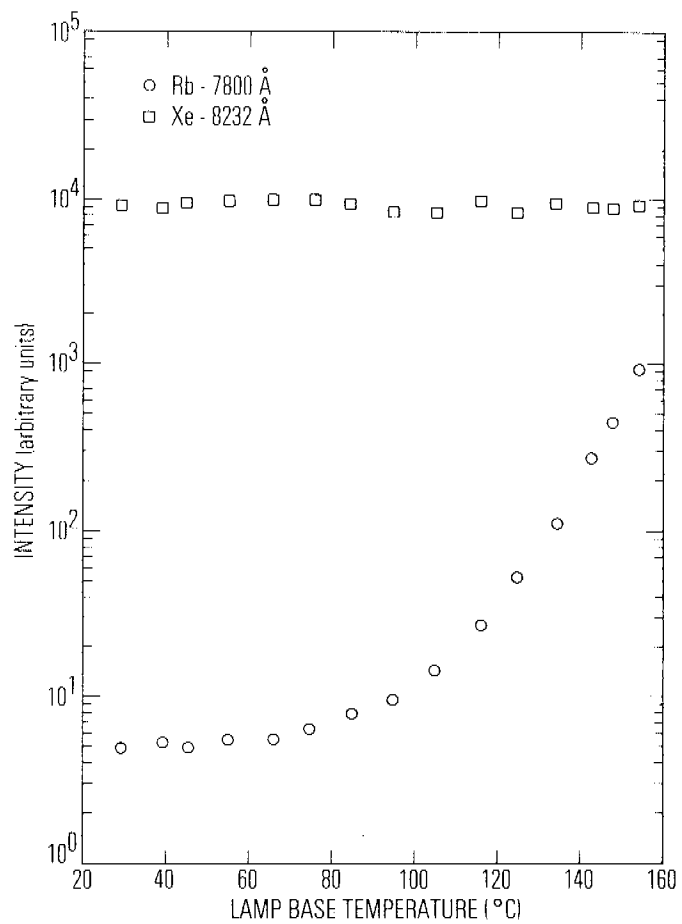


Figure 1b. Emission intensities for Rb 7800Å line ( $\circ$ ) and Xe 8232Å ( $\square$ ) for a failed Rb lamp as a function of base temperature



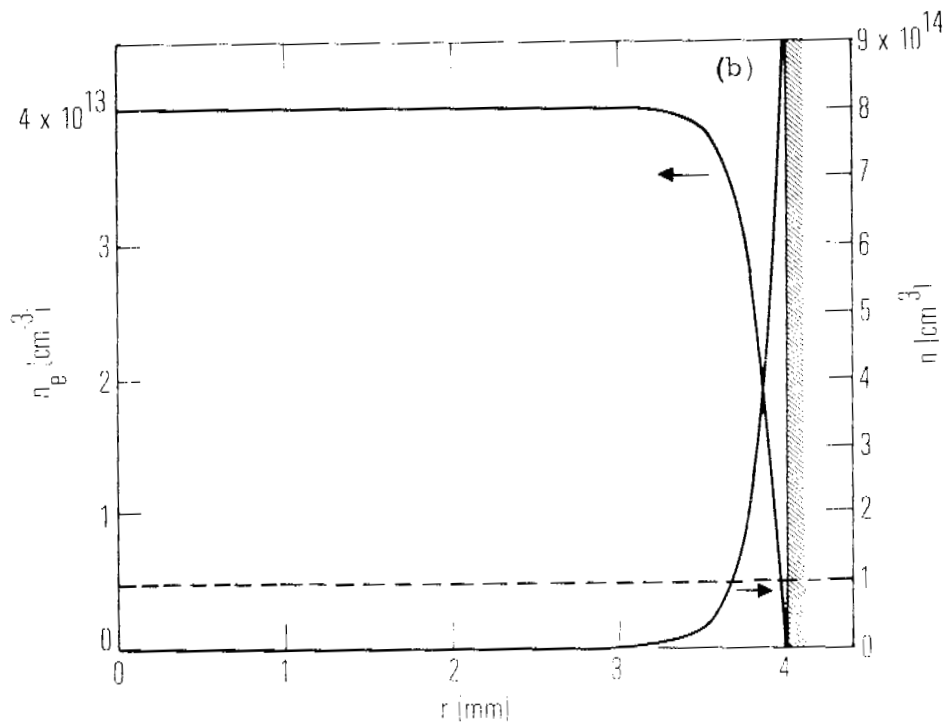
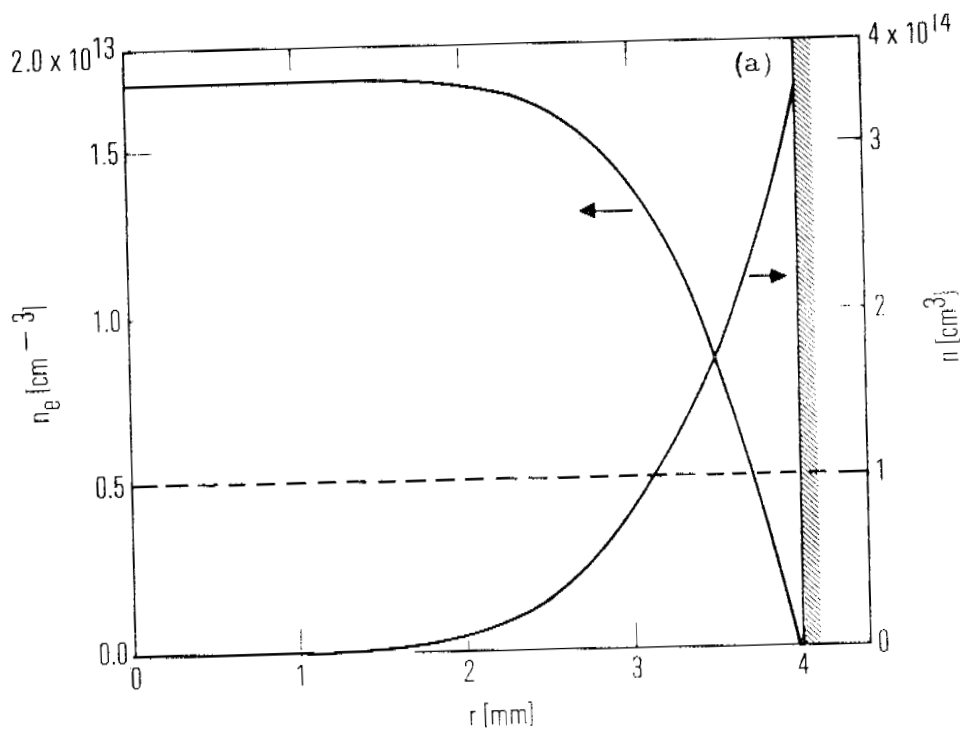


Figure 2. Theoretical calculations of Rb and electron densities as a function of radial position in a plasma discharge for a)  $0.3 \text{ W/cm}$  and b)  $3.0 \text{ W/cm}$  excitation power

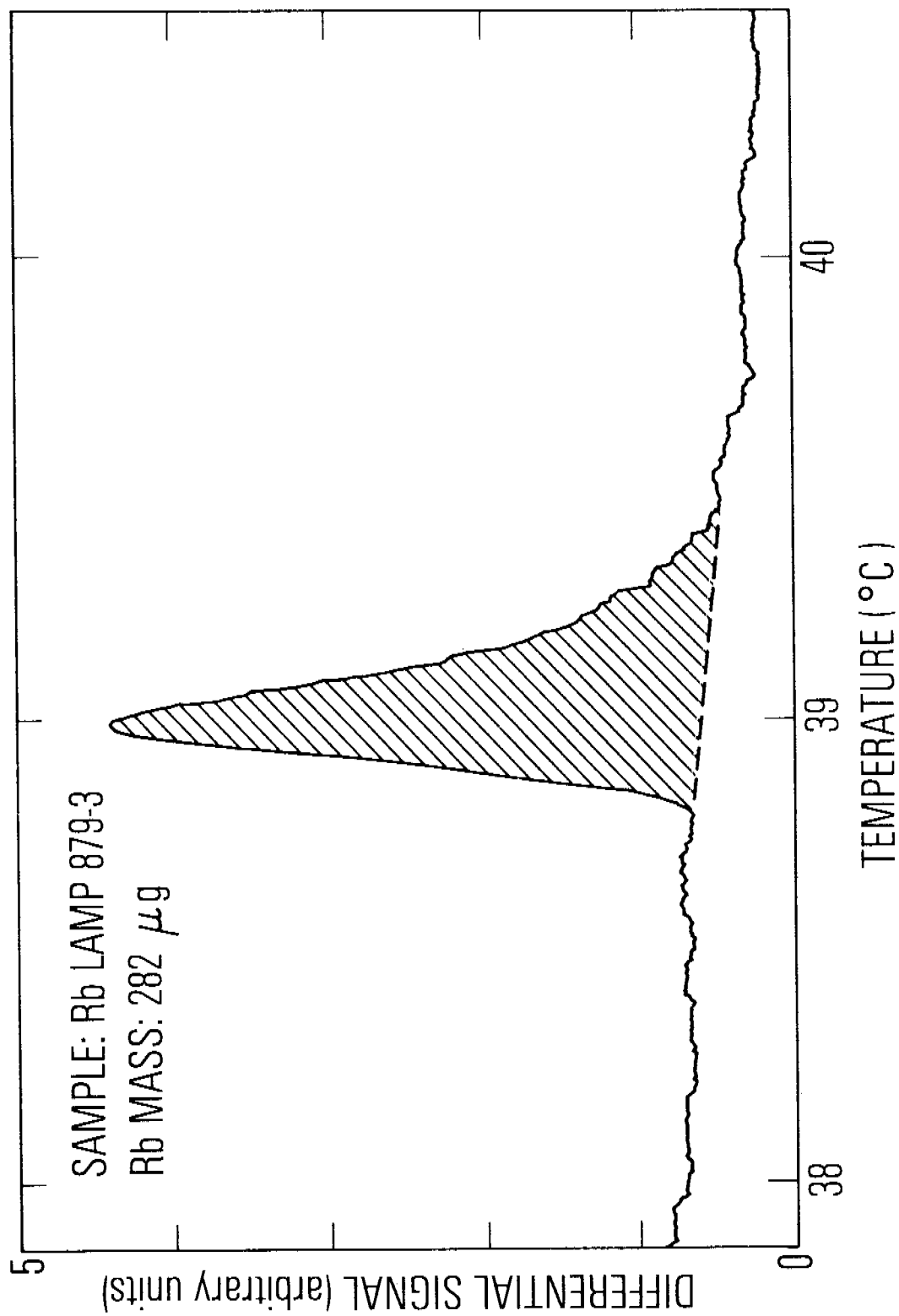


Figure 3. DSC curve for Rb lamp

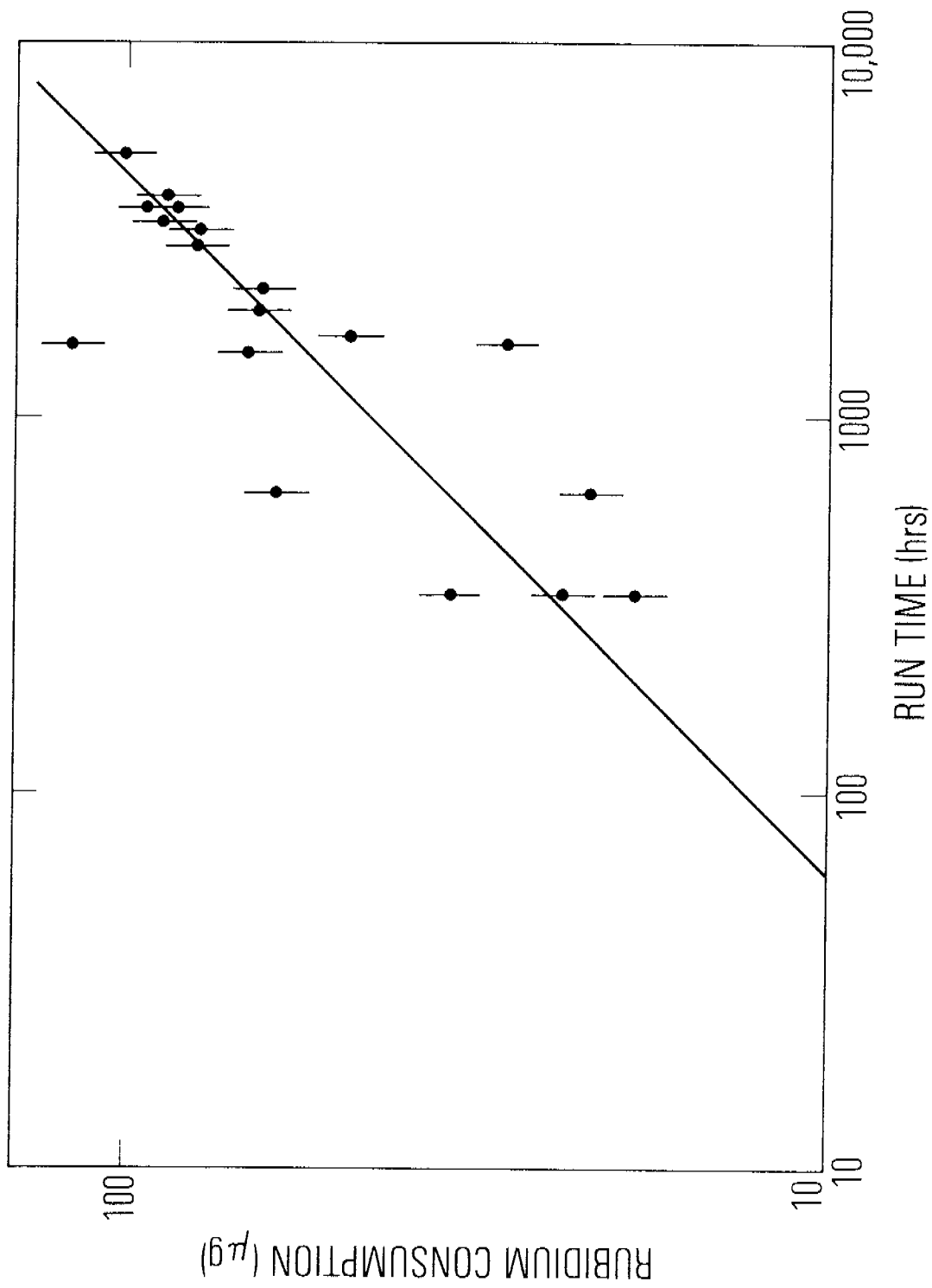


Figure 4. GPS lamp Rb consumption versus operating time

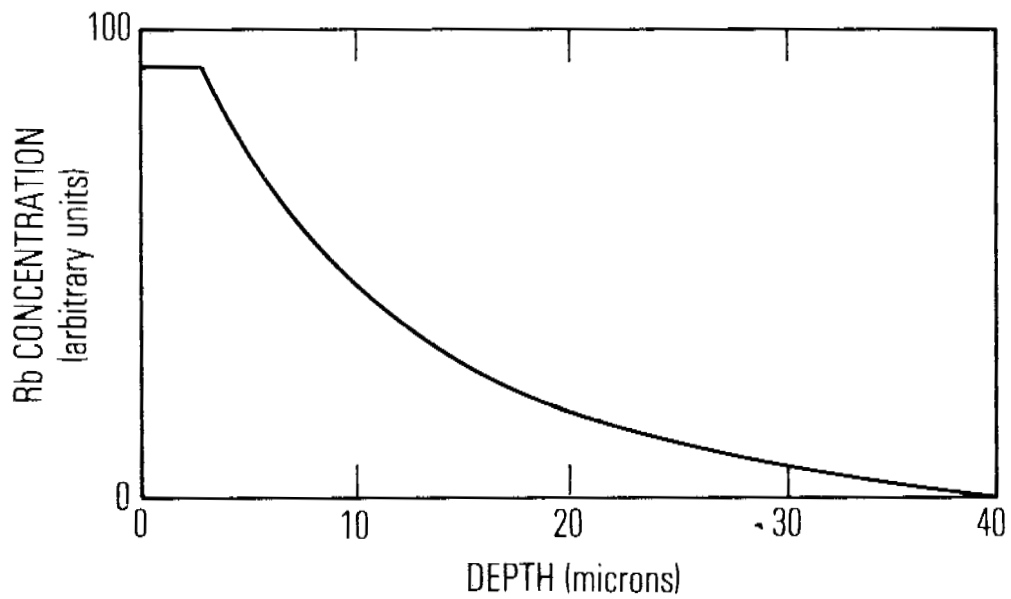
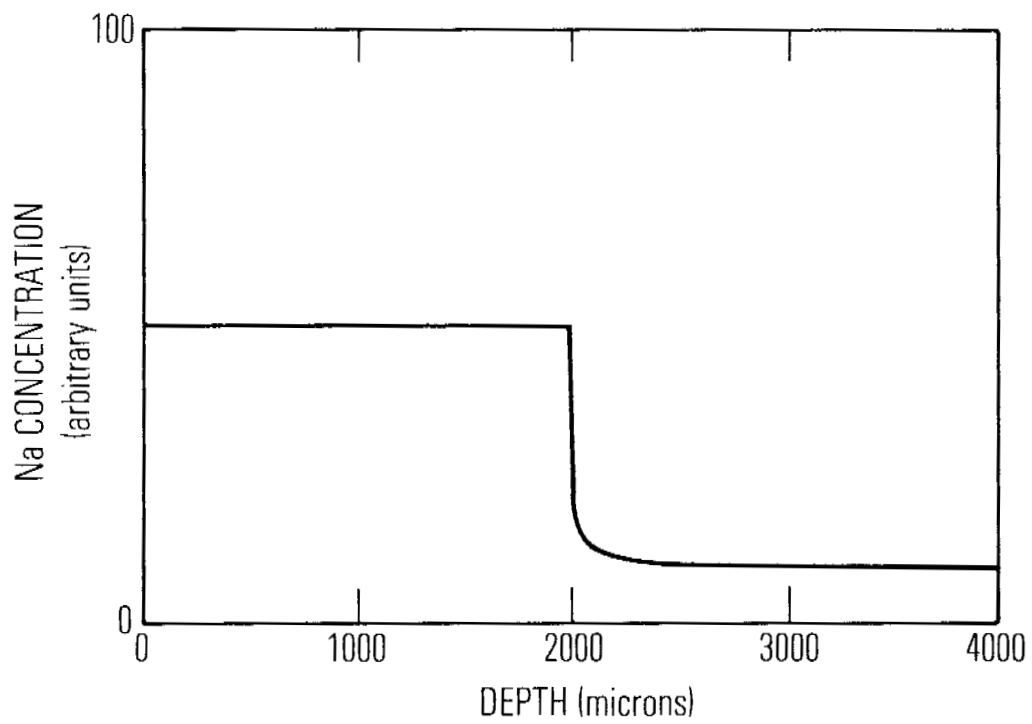


Figure 5. Schematic representation of a) Na and b) Rb penetration profiles into glass

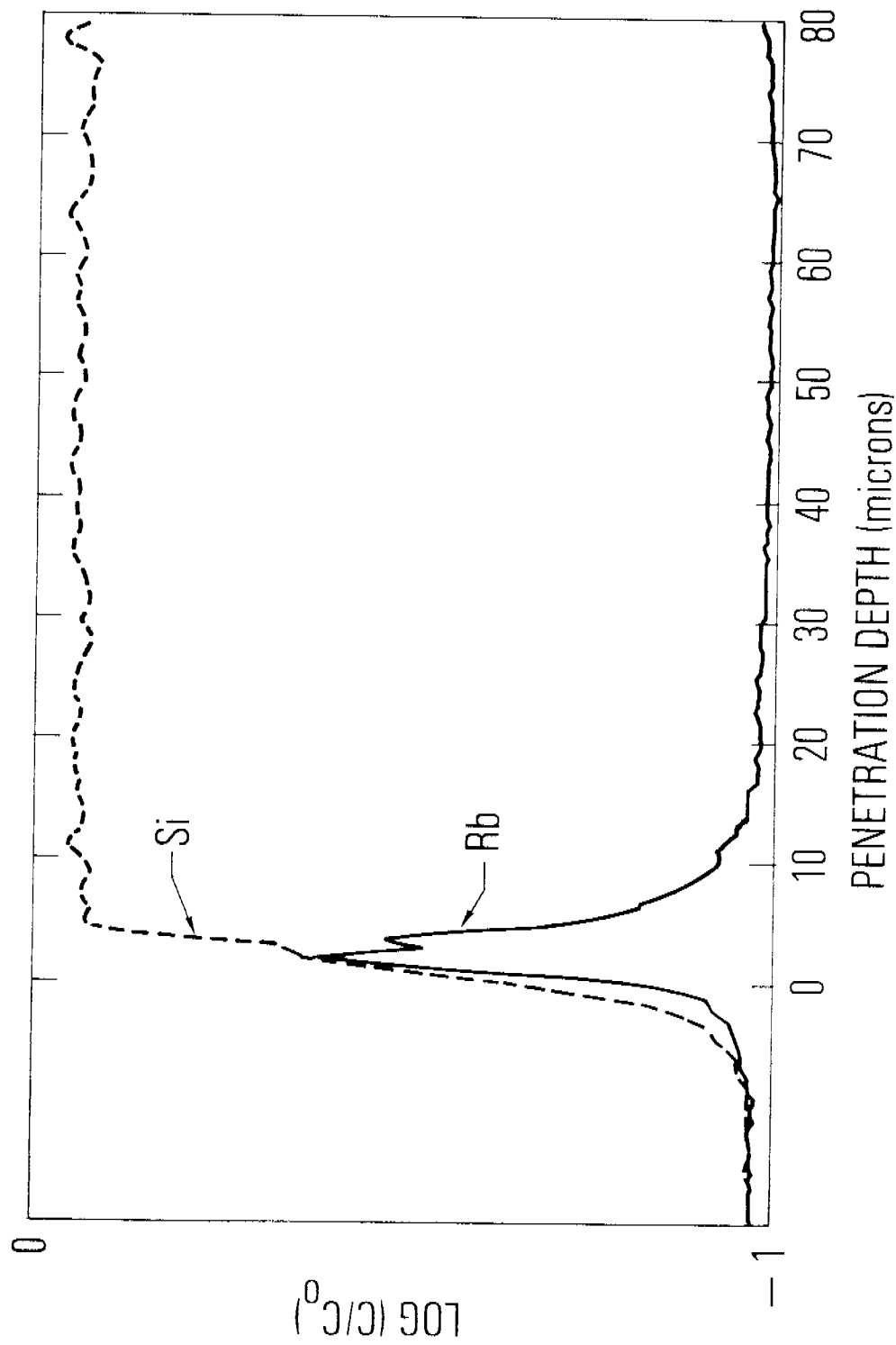


Figure 6. Raw SIMS data for Rb penetration into a pyrex glass surface. The surface occurs at 0 microns. The sharp decrease and increase in Rb concentration near 4 microns is believed to be due to inhomogeneities in the glass and not related to the penetration mechanism

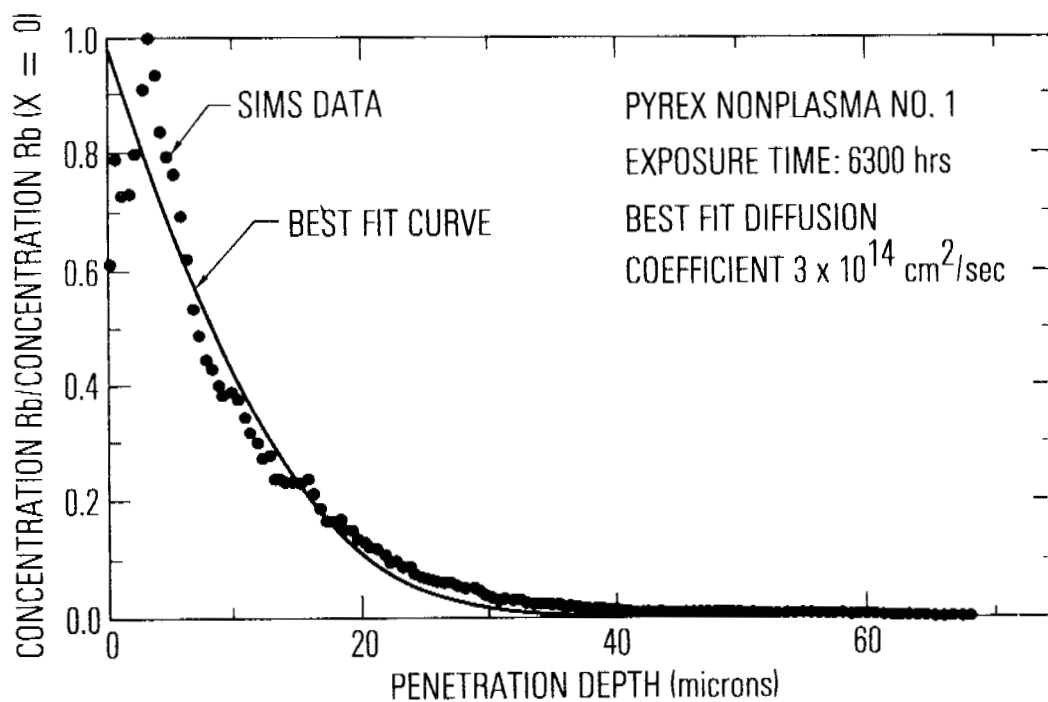
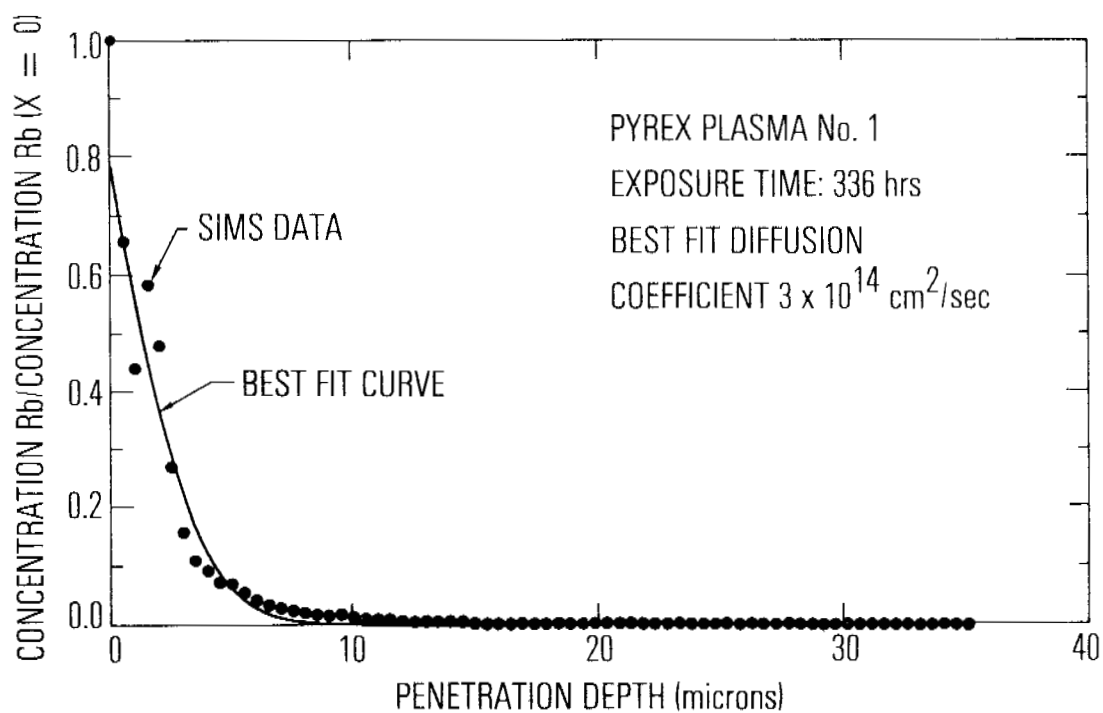


Figure 7. Experimental SIMS data (●) and fit curve (—) for pyrex glass samples a) with discharge present and b) without discharge

## QUESTIONS AND ANSWERS

MR. JOHN VIG, U.S. Army

It seems to me you have the inverse problem that we have in the quartz crystal field. We are worried about diffusing alkali ions out of the quartz to make the quartz more radiation hardened.

And the proposal has been made to grow quartz -- normally it is grown in a sodium hydroxide solution, but the proposal has been made to grow quartz in rubidium hydroxide in order to prevent the incorporation of the alkali into the quartz because apparently rubidium will not go into single crystal quartz.

Has anybody considered the possibility of building lamps out of single crystal quartz?

MR. VOLK:

I have heard it said that if you prepare the quartz correctly, they make much better absorption cells in lamps. However, in our work I have never seen that, which may mean that I don't prepare it correctly. It has been my sort of common experience that quartz is a bad material around rubidium, I don't know.

MR. VIG:

Single crystal quartz?

MR. VOLK:

I would have to check on that. Our techniques though would allow us to look at that rather quickly.

MR. VIG:

It would be interesting.

DR. LUKE MALEKI, Jet Propulsion Laboratory

Could you explain to me -- you had a couple of slides showing the ESCA results and at the end the plasma and non-plasma conditions, comparisons. I am not so sure I understand, when you have the plasma condition, how long do you run it and under what conditions, as opposed to the non-plasma conditions?

On the time scale how is the comparison made?

MR. VOLK:

Well, we ran the non-plasma for much longer. In the plasma it was run for a little over 300 hours and in the non-plasma, just heating with 6300 hours.

It takes a lot longer, of course, to react, that was the whole point of the model, is that you build up this density with the plasma to very large values.

DR. MALEKI:

Okay, maybe I can discuss that with you later.

One other thing, in view of the comment made on this single crystal quartz and so forth. Have you looked into the ion implantation influence in there? That is, the ions, in fact, because of the energy that they have, would --

MR. VOLK:

We don't see any evidence of that, of the ions penetrating, no.

DR. MALEKI:

Okay, thank you.

DR. MICHEL TETU, Laval University, Canada

When the temperature of the lamp is changed the usual observation is that the lamp goes from a ring mode to a pink mode, which means that the temperature is not too high, the density of the rubidium is, as you mentioned, close to the wall of the bulb and you have there a model which seems to explain very well the atomic distribution.

Now, if the temperature is slightly increased, the light seems to come from all over the bulb, which means that you have -- or we observe what we call the pink mode.

Is there any possibility to explain the atomic distribution with your model?

MR. VOLK:

Not at the present, we are working on that. Our model doesn't change modes, unfortunately.

MR. KUHNLE:

Thank you very much.